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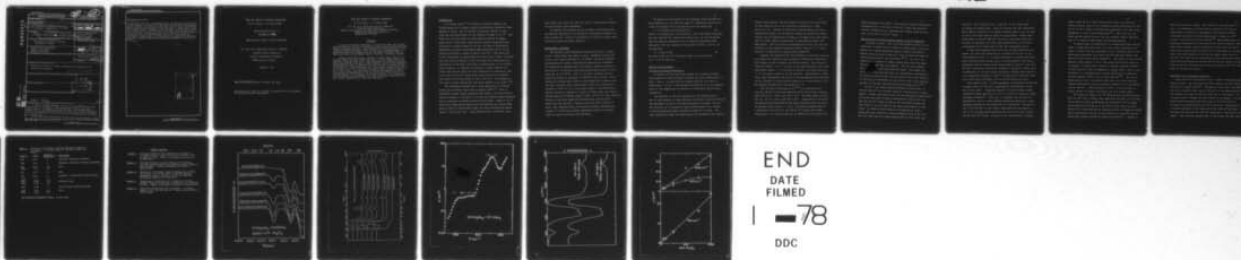
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20. Abstract continued

as those doped with GeO_2 . Unlike As_2Se_3 glass, at impurity concentrations up to 1000 ppm As_2O_3 , 0.5 As_2Se_3 -0.5 GeSe_2 glass exhibits only one major oxide impurity species, characterized by absorption bands at 780 and 1260 cm^{-1} and due to oxygen bonded to network Ge. The observation of a much weaker network As-O vibration band at 670 cm^{-1} confirms that oxygen bonds preferentially to Ge in this glass. The same minor oxide species appears to determine excess IR absorption at the CO_2 laser wavelength of 10.6 μm in both As_2Se_3 and 0.5 As_2Se_3 -0.5 GeSe_2 glasses. The frequencies and intensities of absorption bands due to hydrogen impurities are also quite comparable for these two materials.

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BULK AND IMPURITY INFRARED ABSORPTION
IN 0.5 As₂Se₃ - 0.5 GeSe₂ GLASS

Technical Report No. 35

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October, 1977

*Now with Corning Glass, Corning, New York.

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BULK AND IMPURITY INFRARED ABSORPTION

IN 0.5 As₂Se₃ - 0.5 GeSe₂ GLASS

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ABSTRACT

A study of infrared absorption in the 250 to 4000 cm⁻¹ region has been carried out for 0.5 As₂Se₃-0.5 GeSe₂ glasses quantitatively doped with oxide impurity. The frequencies of the intrinsic 2- and 3-phonon absorption bands at 490 and 690 cm⁻¹ correspond well to those predicted from combinations of the high frequency bands in the first order IR and Raman spectra of As₂Se₃ and GeSe₂ glasses.

Glasses doped with As₂O₃ exhibit the same oxide impurity absorption bands as those doped with GeO₂. Unlike As₂Se₃ glass, at impurity concentrations up to 1000 ppm As₂O₃, 0.5 As₂Se₃-0.5 GeSe₂ glass exhibits only one major oxide impurity species, characterized by absorption bands at 780 and 1260 cm⁻¹ and due to oxygen bonded to network Ge. The observation of a much weaker network As-O vibration band at 670 cm⁻¹ confirms that oxygen bonds preferentially to Ge in this glass. The same minor oxide species appears to determine excess IR absorption at the CO₂ laser wavelength of 10.6 μm in both As₂Se₃ and 0.5 As₂Se₃ -0.5 GeSe₂ glasses. The frequencies and intensities of absorption bands due to hydrogen impurities are also quite comparable for these two materials.

INTRODUCTION

In a recent paper (1) we reported a study of impurity infrared absorption in As_2Se_3 glasses quantitatively doped with small amounts of As_2O_3 . One of the more interesting results of that study was the verification of the findings of Vasko et al. (2) that there were two main types of oxide impurity species in As_2Se_3 glass: Form I tentatively identified as discrete As_4O_6 molecules and having a strong IR band at 785 cm^{-1} and Form II tentatively identified as oxygen incorporated substitutionally for Se in the network and having a strong IR band at 650 cm^{-1} . The variations in the intensities of these bands with total As_2O_3 content indicated that the relative amounts of the two oxides were controlled by an equilibrium in the melt, with Form II predominating at low overall oxide contents. In addition the presence in small amounts of a third oxide species (Form III) was indicated by an absorption band in the 930 to 970 cm^{-1} region whose intensity did not correlate with those of the oxide bands at 650 or 785 cm^{-1} . The presence of two types of oxide species has also been reported in Se glass (3,4).

The IR absorption bands due to oxide impurities in Ge-As-Se glasses are different from those in As_2Se_3 glass (5-7). This is presumably because oxygen preferentially bonds to the most electro-positive element in the melt (7), so that the observed oxide bands are due to vibrations of groups containing Ge-O bonds. Vasko et al. (2) found that GeSe_9 glasses doped with GeO exhibited one strong oxide band at 780 cm^{-1} , while GeSe_9 doped with GeO_2 exhibited two strong bands at 780 and 887 cm^{-1} . This suggested that in Ge-As-Se glass

there might also exist more than one type of oxide species bonded to the principal glass components.

To explore this possibility and to better characterize bulk and impurity absorption in Ge-containing chalcogenide glasses, we have carried out a study of IR absorption in Ge-As-Se glasses quantitatively doped with oxide impurity.

EXPERIMENTAL PROCEDURE

The Ge-As-Se glass composition studied was 50 mol % As_2Se_3 -50 mol % GeSe_2 doped with As_2O_3 or GeO_2 . Elemental starting materials were Cominco American As (99.9999%), Atomergic Chemicals Ge (semiconductor grade), and Atomergic Chemicals Se (99.9999%). The glasses were prepared using the general procedure described previously⁽¹⁾ by melting 15g batches sealed under vacuum in Vycor tubes for 20 h at 940°C. Prior to filling, the Vycor reaction tubes were baked out overnight at 850-900°C under vacuum. After melting the glasses were cooled to room temperature, removed from the Vycor reaction tubes, sealed under vacuum into Pyrex tubes, annealed at 215°C for 2 h, and cooled slowly to room temperature. Several batches of undoped 0.5 As_2Se_3 -0.5 GeSe_2 glass and several batches doped with 1000 ppm As_2O_3 (1 ppm = 10^{-4} mol %) were prepared, along with one batch doped with 500 ppm As_2O_3 and one batch doped with 1000 ppm GeO_2 . Glasses containing other amounts of As_2O_3 were prepared using the dilution procedure described previously⁽¹⁾ by melting together appropriate amounts of undoped glass and glass containing 1000 ppm As_2O_3 .

IR spectra of the glasses in the frequency range 250-4000 cm^{-1} were measured as in our previous paper⁽¹⁾. Absorption coefficients α were calculated from the IR spectra using the expression

$$T = (1-R)^2 \exp(-\alpha x) / [1-R^2 \exp(-2\alpha x)] \quad (1)$$

where T is transmission, R reflectivity, and x the sample thickness. For each spectrum the reflectivity used in Eq. (1) was determined from the apparent transmission T_0 in regions of negligible bulk absorption (the flat regions of the spectra of Figs. 1 and 2) via the equation:

$$R = (1-T_0)/(1+T_0) \quad (2)$$

The mean value of R for 12 spectra taken in this study was 0.21 ± 0.02 at 1400 cm^{-1} .

RESULTS AND DISCUSSION

Intrinsic Multiphonon Absorption

IR spectra of thin and thick samples of $0.5 \text{ As}_2\text{Se}_3$ - 0.5 GeSe_3 glass doped with varying amounts of As_2O_3 are shown respectively in Figs. 1 and 2. In each case the topmost spectrum is of the undoped glass. In Fig. 3 the absorption coefficient α of the undoped glass at low frequencies is plotted on a logarithmic scale versus frequency $\bar{\nu}$.

The shoulder at 780 cm^{-1} exhibited by the undoped glass is due to trace amounts of oxide impurity (see below), but below 740 cm^{-1} the absorption is due to intrinsic multiphonon processes (1,8-10). The structure of $0.5 \text{ As}_2\text{Se}_3$ - 0.5 GeSe_2 glass consists of a network of AsSe_3 pyramids and GeSe_4 tetrahedra bridged by Se atoms. The high coordination AsSe_3 and GeSe_4 groups are presumably only loosely

coupled vibrationally, and the highest frequency first order bands of this glass are due to the stretching vibrations of these groups (11,12). Because of this loose coupling between the high coordination groups, the multiphonon absorption frequencies should consist only of combinations of AsSe_3 or of GeSe_4 first order bands, with no "mixed" bands corresponding to combinations of AsSe_3 with GeSe_4 bands. This is borne out experimentally by the fact that the intensity of the 2-phonon absorption band at 490 cm^{-1} is a linear function of composition in As_2Se_3 - GeSe_2 glasses (8).

Lucovsky and Galeener (9,12) have proposed an empirical selection rule scheme for predicting the multiphonon combination frequencies which appear in the IR spectra of network glasses. They assign an "activity factor" (+ or -) to each of the high frequency first order vibrational bands, "+" if the band is strong in the Raman spectrum, "-" if the band is strong in the IR spectrum. Combinations of these first order frequencies are strong in the multiphonon Raman spectrum if the "product" of their activity factors is "+" and strong in the multiphonon IR spectrum if the product is "-".

From the data of Lucovsky et al. (13) the frequencies and activity factors of the high frequency first order bands in As_2Se_3 glass are $217(-)$, $239(+)$ and $270(-) \text{ cm}^{-1}$. For GeSe_2 glass they are $201(+)$, $219(+)$, $254(-)$ and $320(-) \text{ cm}^{-1}$. Frequencies of IR active multiphonon bands predicted by the above selection rules are shown as vertical lines in Fig. 3. (E.g., the lowest frequency band is a combination of the $217(-)$ and $239(+)$ cm^{-1} As_2Se_3 first order frequencies.) No "mixed" bands due to combinations of As_2Se_3 with

GeSe₂ frequencies are shown. The predicted 2-phonon frequencies correspond well to the peak at 490 cm⁻¹, while the predicted 3-phonon frequencies are clustered most closely about the plateau in the 650 to 730 cm⁻¹ region.

Absorption Due to Oxide Impurity Bonded to Bulk Components

As shown in Figs. 1 and 2 the most prominent effect of introduction of oxide into 0.5 As₂Se₃-0.5 GeSe₂ glass is the production of a strong absorption band at 780cm⁻¹ along with a medium intensity band at 1260 cm⁻¹, both of which have been documented previously in the literature (5-7). In Fig. 4 IR spectra of 0.5 As₂Se₃-0.5 GeSe₂ glasses doped with 1000 As₂O₃ and with 1000 ppm GeO₂ are compared. The two oxide dopants give rise to the same oxide impurity bands. This shows that during the melting process there is considerable rearrangement of chemical bonds and that the final form of the oxide impurity in the glass is independent of its initial form in the reaction mixture, as has been found previously for As₂Se₃ glass^(2,14).

In Fig. 5 the oxide impurity absorption coefficients at 780 and 1260 cm⁻¹ are plotted versus the concentration of As₂O₃ dopant. Within experimental error the two absorption coefficients are linear functions of As₂O₃ concentration, showing that the 780 and 1260 cm⁻¹ bands are due to the same oxide species and that there is only one form of the major oxide species in this glass. One type of oxide impurity in As₂Se₃ glass (Form I, As₄O₆ molecules) exhibits a strong absorption band at 785 cm⁻¹, but this same form also shows weaker bands at 1050, 1265, and

1340 cm^{-1} , two of which are not observed in the oxide doped 0.5 As_2Se_3 -0.5 GeSe_2 glass. Hence we conclude that the predominant oxide impurity species in 0.5 As_2Se_3 -0.5 GeSe_2 glass is not the same as any of the oxide impurity forms in As_2Se_3 glass. Rather these oxide bands at 780 and 1260 cm^{-1} are due to Ge-O bond vibrations, so that, as expected, the oxide bonds preferentially to the more electropositive Ge rather than to the less electropositive As.

A weak oxide impurity band, which has not been previously reported, for Ge-As-Se glasses may be observed at 670 cm^{-1} in the thick samples of Fig. 2. It seems reasonable to identify this band with vibrations of As-O bonds, since in As_2Se_3 glass⁽¹⁾ the strong absorption band of network oxide (As_2O_3 Form II) occurs at 650 cm^{-1} . The small intensity of this band in doped 0.5 As_2Se_3 -0.5 GeSe_2 glass in comparison to its much larger intensity in As_2Se_3 glass containing a comparable amounts of oxide⁽¹⁾ reinforces the conclusion that very little oxide is bonded to As in the Ge-containing glass.

Also shown in Fig. 5 is the dependence of absorption coefficient on As_2O_3 content at 940 cm^{-1} , approximately the frequency of the 10.6 μm CO_2 laser. Comparable amounts of oxide produce roughly comparable excess absorption at 10.6 μm in both 0.5 As_2Se_3 -0.5 GeSe_2 and As_2Se_3 glasses⁽¹⁾. From Fig. 2 it appears that the 940 cm^{-1} absorption is due to a weak impurity band which appears as a high frequency shoulder on the strong 780 cm^{-1} oxide band. The plot in Fig. 5 for 940 cm^{-1} is not linear, suggesting that this band is not due to the same oxide species giving rise to the more intense 780 and 1260 cm^{-1} bands. As noted in the Introduction, in As_2Se_3

glass a band due to a minor oxide species (Form III) which was clearly distinct from the two predominant oxide forms occurs in the 930 to 970 cm^{-1} region; this band also exhibited a less than linear dependence on total oxide concentration⁽¹⁾. The nature of this oxide species remains unclear, but the evidence clearly indicates that it is common to both As_2Se_3 and Ge-As-Se glasses.

In As_2Se_3 glass the appearance of a second major oxide species (Form I, As_4O_6 molecules) after the total oxide concentration exceeds a certain level was considered to be a precursor step to the gross phase separation into oxide-rich and oxide-poor phases that occurs at high overall oxide content⁽¹⁾. That there is only one predominant oxide species in this same oxide concentration range in 0.5 As_2Se_3 -0.5 GeSe_2 glass indicates a greater chemical affinity of this glass for oxide in comparison to As_2Se_3 glass. This is also reflected in a correspondingly enhanced difficulty in preparing Ge-As-Se glasses totally free of oxide impurity⁽¹⁵⁾. For the undoped glass of Fig. 3 we estimate that the tail of the intrinsic 3-phonon absorption plateau contributes roughly half of the absorption at 780 cm^{-1} . This translates via Fig. 5 into an oxide impurity content of roughly 8 ppm As_2O_3 for this undoped glass.

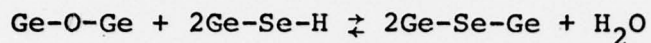
The reason why Vasko et al.⁽²⁾ observed only one strong oxide band (at 780 cm^{-1}) in GeSe_9 glass doped with 500 ppm O_2 in the form of GeO and two strong oxide bands (at 780 and 887 cm^{-1}) in GeSe_9 glass doped with 500 ppm O_2 in the form of GeO_2 remains unclear. The 887 cm^{-1} oxide band was not observed in the 0.5 As_2Se_3 -0.5 GeSe_2 glass studied here, nor has it been observed in the oxide contaminated GeSe_4 glasses studied by Savage and Nielson⁽⁵⁾. Indeed, in

view of our previous remarks and evidence of the type shown in Fig. 4, no dependence of oxide impurity spectra on the type of oxide dopant is expected in homogeneous chalcogenide glasses. A possible explanation for the observations of Vasko et al.⁽²⁾ is that, like sulfur-rich Ge-S glasses⁽¹⁶⁾, their GeSe₉ glass is segregated microscopically into Ge-rich and Se-rich regions. Some uncontrolled thermal history difference between their two oxide-doped GeSe₉ glasses might then have led to confinement in one case of all the oxide impurity in the Ge-rich phase (giving only the 780 cm⁻¹ Ge-O band) and to partitioning in the second case of the oxide impurity between the Ge-rich and the Se-rich regions (giving both the 780 cm⁻¹ Ge-O band and an additional band at 887 cm⁻¹ from oxide in the Se-rich region).

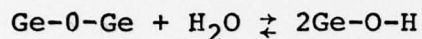
Absorption Due to Hydrogen Impurities

Above 1400 cm⁻¹ the glasses of Fig. 2 exhibit various hydrogen impurity bands. The same bands at almost exactly the same frequencies occur in As₂Se₃ glass⁽¹⁾. The bands at 1590, 3510, and 3590 cm⁻¹ are due to molecular H₂O, that at 3470 cm⁻¹ to -OH groups bonded to the network, and those at 2200 and 2450 cm⁻¹ to -SeH groups. As in As₂Se₃ glass, increase of oxide content in 0.5 As₂Se₃ - 0.5 GeSe₂ glass causes the double band due to H₂O at 3510 and 3590 cm⁻¹ to merge into single band due to -OH at 3470 cm⁻¹, accompanied by a relative decrease in the intensity of the 1590 cm⁻¹ H₂O band. At the same time the 2200 and 2450 cm⁻¹ bands due to -SeH tend to disappear. This behavior suggests that in this glass the small amount

of hydrogen present in the melt components competes successfully with the Ge for the available oxide. Addition of a small amount of oxide to the melt produces water by driving to the right the local bond reaction



Further oxide additions produce -OH groups by driving to the right the subsequent reaction



In Table I all the absorption bands of 0.5 As₂Se₃ - 0.5 GeSe₂ glass identified in this study are listed and categorized.

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Table I. Intrinsic and impurity infrared absorption bands in 0.5 As₂Se₃ - 0.5 GeSe₂ glass in the 250 to 4000 cm⁻¹ region.

$\bar{\nu}(\text{cm}^{-1})$	$\lambda(\mu\text{m})$	Relative Intensity ^(a)	Assignment
490	20.4	s	intrinsic 2-phonon processes
700	14.3	m	shoulder, intrinsic 3-phonon processes
780	12.8	s }	Ge-O
1260	7.9	m }	
670	14.9	w	As-O
930	10.8	w	shoulder, unidentified oxide species
1590	6.3	w }	molecular H ₂ O
3510	2.85	w }	
3590	2.79	w }	
3470	2.88	w	O-H in oxide containing glass
2200	4.55	w }	Se-H
2450	4.08	vw }	

(a) s-strong, m-medium, w-weak, vw-very weak

FIGURE CAPTIONS

- Figure 1. Infrared spectra of thin samples of 0.5 As₂Se₃ - 0.5 GeSe₂ glasses doped with various amounts (shown in ppm) of As₂O₃. Sample thicknesses are given in parentheses.
- Figure 2. Infrared spectra of thick samples of 0.5 As₂Se₃ - 0.5 GeSe₂ glasses doped with various amounts (shown in ppm) of As₂O₃. Sample thicknesses are given in parentheses.
- Figure 3. Absorption coefficient versus frequency for undoped 0.5 As₂Se₃ - 0.5 GeSe₂ glass in the multiphonon absorption region. Vertical lines are predicted multiphonon absorption frequencies.
- Figure 4. Comparison of IR spectra of 0.5 As₂Se₃ - 0.5 GeSe₂ glasses doped with 1000 ppm of As₂O₃ and with 1000 ppm of GeO₂. Sample thicknesses are given in parentheses.
- Figure 5. Absorption coefficients of 0.5 As₂Se₃ - 0.5 GeSe₂ glass at 780, 940 and 1260 cm⁻¹ versus concentration of As₂O₃ dopant.

